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✓ This report describes a unique instrumental facility where chemically-assisted crack propagation can be studied; i.e. crack-velocity/stress intensity measurements can be made in the presence of specific environments, and the fracture surfaces so created can be analyzed, in-situ, using a neutral beam static SIMS technique. The report also summarizes studies of slow crack growth, corrosion and fatigue of fluorozirconate glasses. JTS

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INTRODUCTION

This report summarizes the work performed at The Pennsylvania State University during the period 1 March 1986 to 28 February 1988. The program was directed by Professor Carlo G. Pantano; Professor Jack J. Mecholsky, research associate Cheryl Houser and graduate students Armando Gonzalez, Andrew Phelps and Alen Then were co-investigators.

The major objective of this program was the design and construction of an instrumental facility where the surface phenomena associated with fracture and slow crack growth can be studied. The secondary objective of this program was the study of fracture and slow crack growth in fluoride and chalcogenide infrared transmitting glasses. A summary of these research studies is provided in this report; a list of the resulting theses, publications and presentations is also included.

SUMMARY OF ACCOMPLISHMENTS

Theses

"Slow Crack Growth in Fluorozirconate Glass" by Armando Gonzalez, M.S. Thesis, 1987.

"Fatigue Behavior in Fluorozirconate Glass" by Alan Then, B.S. Thesis, 1987.

"The Effect of Crack Size on the Stress Corrosion Process in Soda-Lime-Silica Glass" by James Bonner, B.S. Thesis, 1987.

"Surface Layer Formation During the Aqueous Corrosion of Fluorozirconate Glass" by Andrew Phelps, M.S. Thesis, 1988.

Publications

1. "Surface Chemistry and Slow Crack Growth Behavior of Fluorozirconate Glass" by Carlo G. Pantano, in Halide Glasses for Infrared Fiber Optics, (Rui Almeida, Editor, NATO ASI Series, Nijhoff Publ, Netherlands, 1987) pp. 199-218.

2. "Mechanical Properties of IR Glasses and Fibers" by J.J. Mecholsky, J.A. Wysocki, and C. G. Pantano, SPIE, 843, 21 (1987).

3. "Fractoemission from Fused Silica and Sodium-Silicate Glasses" by J.T. Dickinson, S.C. Langford, L.C. Jensen, G.L. McVay, J.F. Kelso and C. G. Pantano, J. Vac. Sci. Technol., A6(3), 1084 (1988).

4. "Hydrolysis Reactions at the Surface of Fluorozirconate Glasses" by C. G. Pantano and R. K. Brow, J. Amer. Ceram. Soc., 71 (7), 577 (1988).

5. "Structural Changes in Stressed As₂S₃ Glass Fibers Determined by Raman Spectroscopy" by D.S. Knight, J.J. Mecholsky and W.B. White, J. Am. Ceram. Soc., 70(8), 561 (1987).

Presentations

"Surface Chemistry and Slow Crack Growth in Fluorozirconate Glasses" by Carlo G. Pantano at the NATO Advanced Research Workshop on Fluoride Glasses, Vilamoura, Portugal.

"Surface Analysis of Corroded Fluorozirconate Glass" by Carlo G. Pantano at the 89th Annual Meeting of the American Ceramic Society.

"Slow Crack Growth in Fluoride Glass" by Armando Gonzalez at the 89th Annual Meeting of the American Ceramic Society.

"Electron Spectroscopy in Glass Research" by Carlo G. Pantano at the 89th Annual Meeting of the American Ceramic Society.

"Surface Chemistry and Fracture of Glasses" by Carlo G. Pantano at the AFOSR Workshop on Surface Chemistry, Air Force Academy.

SUMMARY OF RESEARCH

I. Instrumentation for Fracture and Fracture Surface Studies. A unique facility has been developed to study various aspects of the slow crack growth process in glass, and the fracture surfaces so created. The key features are:

- (i) a neutral-beam gun for ion-desorption and static-SIMS of fracture surfaces,
- (ii) a quadrupole mass spectrometer for detection of ionic species desorbed, sputtered or ejected during or after fracture,
- (iii) an electron multiplier for detection of the electrons detected during crack-propagation, and
- (iv) an in-situ fracture device where fracture surfaces can be created under controlled environmental conditions and at any desired velocity.

Figure 1 shows the plan-diagram of the neutral beam static secondary ion mass spectrometer (NPB-Static SIMS), while Figure 2 presents schematic diagrams of the fracture devices. The slow fracture chamber is attached directly to the NPB-Static SIMS chamber (at the gate valve (5) in Figure 1) so that the fracture surfaces can be analyzed without exposure to the atmosphere. The fracture event can also be carried-out in the NPB-Static SIMS chamber (e.g. in front of the mass spectrometer or electron multiplier), but the partial pressure of reactive gas is limited to 10^{-6} or 10^{-7} in this case. Figure 3 presents photographs of the system. It includes an IBM/AT computer for processing the velocity-stress intensity (V-K) diagrams, the SIMS spectra, and the ionic/electronic fractoemissions.

The neutral-beam static SIMS is ideally suited to fracture surface analyses of glass. The neutral-beam eliminates the charging problems which often plague surface studies of glass. The static-SIMS and/or ionic desorption feature provides monolayer sensitivity to inorganic and organic species. Finally, the mass spectrometer provides the capability to use isotropic tracers in the crack growth environment, so that the stress enhanced chemical reaction associated with fracture can be followed. Figures 4a and 4b are example spectra of glass fracture surfaces where the

chemisorption of water (SiOH) is apparent. Figure 5 demonstrates the monolayer sensitivity to organometallic adsorbates on the fracture surface.

Figure 6 illustrates the VK data obtained in the slow fracture chamber at atmospheric pressure and at pressures of 10^{-6} and 10^{-7} torr. It is significant that the traces of water at 10^{-6} and 10^{-7} torr lead to slow crack growth. Thus, the range of crack velocity can be varied over orders of magnitude, and thereby, the kinetics and/or stress-intensity dependences of the crack-tip chemical reactions can be examined on the fracture surfaces.

We have not yet performed any fractoemission studies in this system, but some preliminary experiments were done at Washington State University in collaboration with Prof. Tom Dickinson. The data in Figure 7 reveals that an intense emission of oxygen occurs during the fast fracture of silica and soda-silica glasses. It is noteworthy that the emission persists for several milliseconds after the fracture event. It suggests that a time-dependent recombination of oxygen ions may occur on the fracture surfaces. In the case of the sodium glass, the emission of sodium is also observed. A primary point of interest is whether or not these emissions correspond to the fracture event (bond-breaking) or equilibration of the fracture surfaces (reconstruction). Thus, the new instrument provides the capability to measure the ionic (electronic) fractoemission as a function of the crack velocity and/or the stored strain energy in the crack-tip. These studies are currently in progress.

II. Slow Crack Growth in Fluorozirconate Glass. The subcritical crack growth behavior of a fluorozirconate glass-composition ($Zr_{.13}Ba_{.08}La_{.01}Al_{.01}F_{.76}$) was determined using a constant moment double cantilever beam technique. The tests were conducted in water, ammonia gas, moist nitrogen and various other solvents. All of the environments produced slow crack growth at stress intensities between 0.16 and 0.25 MPa-m^{1/2} where the crack velocities ranged from 10^{-9} to 10^{-2} m/s.

It was found that chemical species which promote crack growth in silicate glass were also active in the case of this fluorozirconate glass. However, the crack growth characteristics of these

two glass systems are quite different. In the fluorides, all of the test environments lead to a well-defined threshold for crack growth. At stress intensities above the threshold, some environments produced region I crack growth (reaction rate limited), and yet others showed only region II (diffusion limited) crack growth. Such behavior is unique to fluorozirconate glass. The most active crack growth agent was water; even in non-aqueous environments, water impurities often controlled crack growth. In these cases, crack velocities scaled with the water activity in the solvent.

It is postulated that as in vitreous silica, crack growth proceeds by a dissociative chemisorption mechanism. Only species with both electrophilic and nucleophilic characteristics were able to promote crack growth consistent with such a mechanism. Further, there is a strong correlation between the type of crack growth (region I or region II) which occurs, and the reaction products that form during the dissociative chemisorption reaction. Environments capable of producing HF surface reaction products did not exhibit region I crack growth. In these cases, region II crack growth was preceded by a distinct threshold.

III. Surface Chemistry of Fluorozirconate Glasses. The surface reaction products associated with the hydrolysis of ZBLA glasses were characterized using x-ray photoelectron spectroscopy (XPS); this reaction is fundamental to corrosion and slow-crack growth in ZBLA glasses. The reaction was found to be localized at Zr-F sites, and the predominant reaction product was a Zr-(hydr)oxyfluoride species. The compositional analysis indicated that the (hydr)oxyfluoride has an oxygen-to-fluorine ratio of ~2-to-5. The Zr3d binding energy of this (hydr)oxyfluoride species was interpreted on the basis of its Pauling charge and this, too, was consistent with a (hydr)oxyfluoride surface species of the form $[\text{ZrO}_2\text{F}_5]$ or $[\text{Zr}(\text{OH})_2\text{F}_5]$. The extent of reaction influences the concentration of oxyfluoride surface species, but not their composition. It is proposed that this (hydr)oxyfluoride is created in all aqueous solutions due to attack of Zr-F bonds by molecular water. The pH-dependent dissolution behavior of ZBLA can thereby be explained based upon the solubility of the (hydr)oxyfluoride surface-species. The

steady-state surface compositions measured on glasses exposed to acid, neutral and basic solutions were in agreement with this model.

The development of surface layers during the aqueous corrosion of a fluorozirconate glass has also been characterized. Since it was already known that aqueous corrosion environments become concentrated in HF during the course of reaction, these studies evaluated the surface layer formation over the range of solution concentrations 0, 10^{-4} , 10^{-3} , 10^{-1} , 3, 6, 12 and 26 molar HF in H_2O . The composition-depth profiles were obtained with secondary ion mass spectroscopy (SIMS) while the layer thickness and morphology were studied in the scanning electron microscope (SEM).

It was found that the surface layers which form during the aqueous corrosion of ZBLA are not hydrated relics of the original glass structure, but rather, are reaction product layers which result due to decomposition of the glass and a localized precipitation/recrystallization of hydrated oxyfluorides and fluorides. The HF concentration influences the solubility and recrystallization kinetics of these reaction products, and thereby, controls the growth rate and morphology of the surface layer.

The primary reactant in the decomposition reaction is molecular water. In an excess of pure water - where the increase in HF concentration is limited - a surface layer composed of amorphous (hydr)oxyfluoride precipitates is created; after long times, this layer evolves well developed ZrF_4 crystallites. In the presence of HF, though, the surface layer becomes richer in Ba, less concentrated in Zr and more crystalline in nature. This is consistent with thermodynamic data which show an increase in the solubility of zirconium (hydr)oxyfluoride and decrease in solubility of BaF_2 at low pH. And at $[HF] > 1M$, the stability of compounds of the type $ZrF_4 \cdot xHF \cdot yH_2O$ creates the most distinctive crystalline surface layers. They are composed of columnar grains whose boundary with the bulk glass is exceedingly sharp. The layer is very permeable, and so, there is little or no barrier to reactant transport. In fact, there is evidence that boundary layers of soluble reaction products in the liquid can control the rate of reaction under static conditions.

It is significant that no alteration or reaction of the glass surface is observed in anhydrous solutions of HF. This verifies the important role of molecular water in the initial decomposition of the glass structure. The penetration of water into the glass does not create a distinct film of hydrated glass because the hydrolysis produces decomposition products which dissolve, precipitate, or recrystallize (locally) behind the advancing water diffusion front. The rates of dissolution, precipitation and recrystallization depend directly upon the HF concentration, and so, in neutral and weakly acidic solutions the boundary between the layer and bulk glass is more diffuse than in the case where high HF concentrations are present. The deprotonation of HF and formation of HF_2^- species are probably critical to the reaction mechanism at high HF concentrations.

The significance of these effects are obvious when one considers that the polishing and handling of fluoride glass optical components often involves contact with aqueous solutions. But it is especially evident where condensation/evaporation phenomena are present - that is, weathering. In this case, limited volumes or layers of surface water may become highly concentrated in HF, and it is under these conditions that degradation and alteration of the surface are most apparent. Altogether, it seems likely that fluoride glass optical components will require protective coatings in most practical applications.

IV. Water Diffusion in Fluorozirconate Glass. One major drawback to the use of fluoride glass in fiber optics is their relatively high reactivity with water. This results in a rapid loss of IR transparency due to the IR absorption of OH and water bands. Although very high rates of reaction have been found for contact with liquid water, past studies have shown low reaction rates with water vapor at temperatures up to 90°C. In this study, ZBLA glass was exposed to water vapor at elevated temperatures to accelerate the reaction and obtain diffusion rates for water.

ZBLA glass, composition 57% ZrF_4 , 36% BaF_2 , 3% LaF_3 , and 4% AlF_3 , was obtained from LeVerre Fluore, France. The glass was cut and polished to a one micrometer diamond paste finish with kerosene used as a lubricant. Some samples were treated in a ^{18}O - ^{16}O atmosphere, and

others were placed in a platinum container and heated in a silica tube furnace with controlled amounts of water vapor in an argon or oxygen flowing gas stream.

Secondary ion mass spectroscopy (SIMS) depth profiles were obtained on a Cameca IMF-3F SIMS, using an ^{18}O -beam to reduce and stabilize surface charging. The sputtering rates were calculated by measuring the crater depth with a profilometer. IR spectra and SEM images were also obtained for a number of samples.

At elevated temperatures, water vapor appears to readily penetrate the polished ZBLA surfaces. In a 275°C treatment with a flowing oxygen atmosphere having less than 10 ppm water vapor, surface penetration of water was seen both in the SIMS H and O profiles and in the infrared OH adsorption bands. The samples that were treated in argon and oxygen atmospheres with water contents up to 38 mole % (at temperatures from 200°C to 310°C) indicate that oxygen may slightly enhance the absorption of water, but it is a minor effect.

Unlike aqueous attack where heavy precipitate layers form, SEM images of the surfaces of the vapor reacted samples show almost no recrystallization. Here, hydrogen, oxygen, and carbon diffuse into the glass surface. Hydrogen, however, was found to penetrate deeper than the other two elements.

In general, there was little change in the distribution of glass species as compared to the untreated polished surface. However, the two samples held at 275°C in the high water content atmosphere showed a decrease in fluorine at the surface. This may indicate HF evolution.

In order to study the kinetics of the water penetration, samples were treated at various times in a 4% water-argon atmosphere at 200°C . For consistency, the depth of penetration was arbitrarily chosen to be the point where the oxygen profile reached 10% of the surface plateau intensity. The reaction depths followed a square root of time dependence indicative of a diffusion process. A simple diffusion model was applied to this data and to data from samples run at other temperatures. The equation is:

$$c = c'[1 - \text{erf} [x/2(Dt)^{1/2}]] \quad (1)$$

where c is the concentration of oxygen (assumed to be proportional to the water concentration), c' is the surface concentration for all $t > 0$, x is the depth, D is the diffusion coefficient, and t is time.

This equation applied with the boundary conditions:

$$c = 0 \text{ for } x > 0 \text{ at } t = 0$$

$$c = c' \text{ for } x = 0 \text{ at } t > 0$$

for diffusion in a semi-infinite medium.

In the case of vapor diffusion, these conditions appear to be satisfied. The samples are relatively free of water before treatment and the oxygen profiles increase in depth with time but the surface intensity is relatively constant for a constant water level in the flowing ambient. For 200°C, this yields a value $D = 1.5 (10)^{-17} \text{ cm}^2\text{s}^{-1}$.

Diffusion coefficients were also calculated for samples at other temperatures in order to obtain an activation energy for the diffusion process. The activation energy, E_a , can be obtained from:

$$D = D_0 e^{-E_a/RT} \quad (2)$$

This yields a value for E_a of 97 kJ/mole, which agrees well with an activation energy of 95 kJ/mole found by others for OH diffusion in barium-thorium fluoride glass. The relatively high activation energy also explains why water vapor penetration is not observed at lower temperatures. Using the data here, OH would penetrate less than 0.5 nm after an hour in 90°C vapor!

V. Fatigue Behavior in Fluorozirconate Glass Fiber. The design and fabrication of heavy-metal fluoride optical glass fibers has received much attention in recent years due to their potential as ultra-low and high radiation resistant communication fiber. But the mechanical properties of this family of glasses have not been well studied. This study examined the strength and fatigue characteristics of ZBLAN (zirconium barium-lanthanum-aluminum-sodium fluoride) optical glass fiber obtained from British Telecom. The fiber was studied using dynamic fatigue and fracture surface analysis of fibers tested in uniform tension. The fiber was uncoated.

The inert strength of the fiber was determined to be 146.9 MPa. The correlation parameter between mirror size and tensile strength at failure was determined to be .666 MPa/m. The fatigue parameters were 29 and 4.76 for N and ln B respectively. Lifetime predictions were made on the basis of these fatigue parameters. However, more recent studies have indicated that fluoride glasses display no region 1 crack growth in air. Thus, the appropriateness of dynamic fatigue measurements for characterizing the fatigue behavior of these glasses may be in question.

NPB STATIC SIMS

NEUTRAL PRIMARY BEAM STATIC SECONDARY ION MASS SPECTROMETER

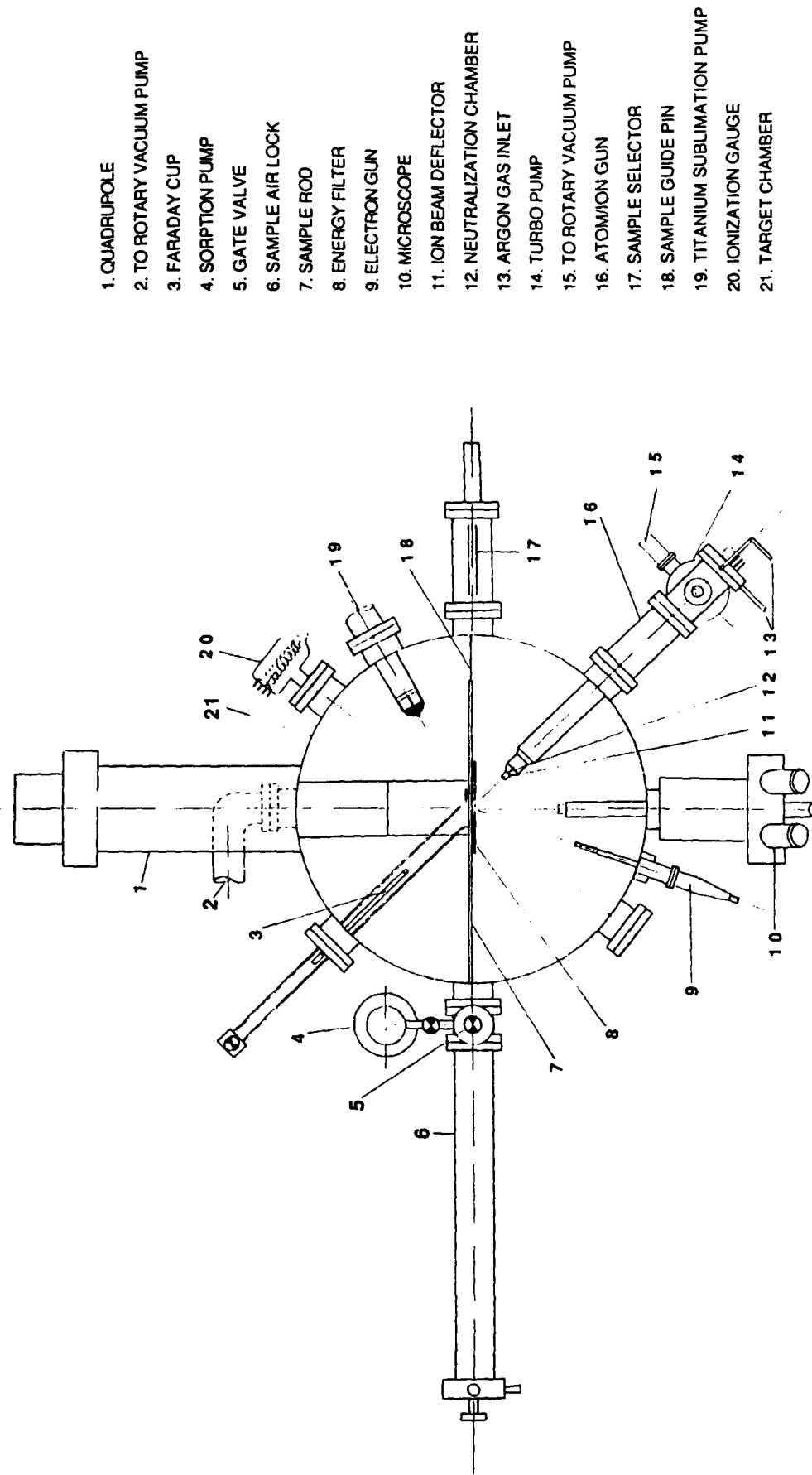


Figure 1. Schematic diagram (top-view) of the ultra-high vacuum chamber for fracture surface studies of glass.

Slow Fracture Chamber

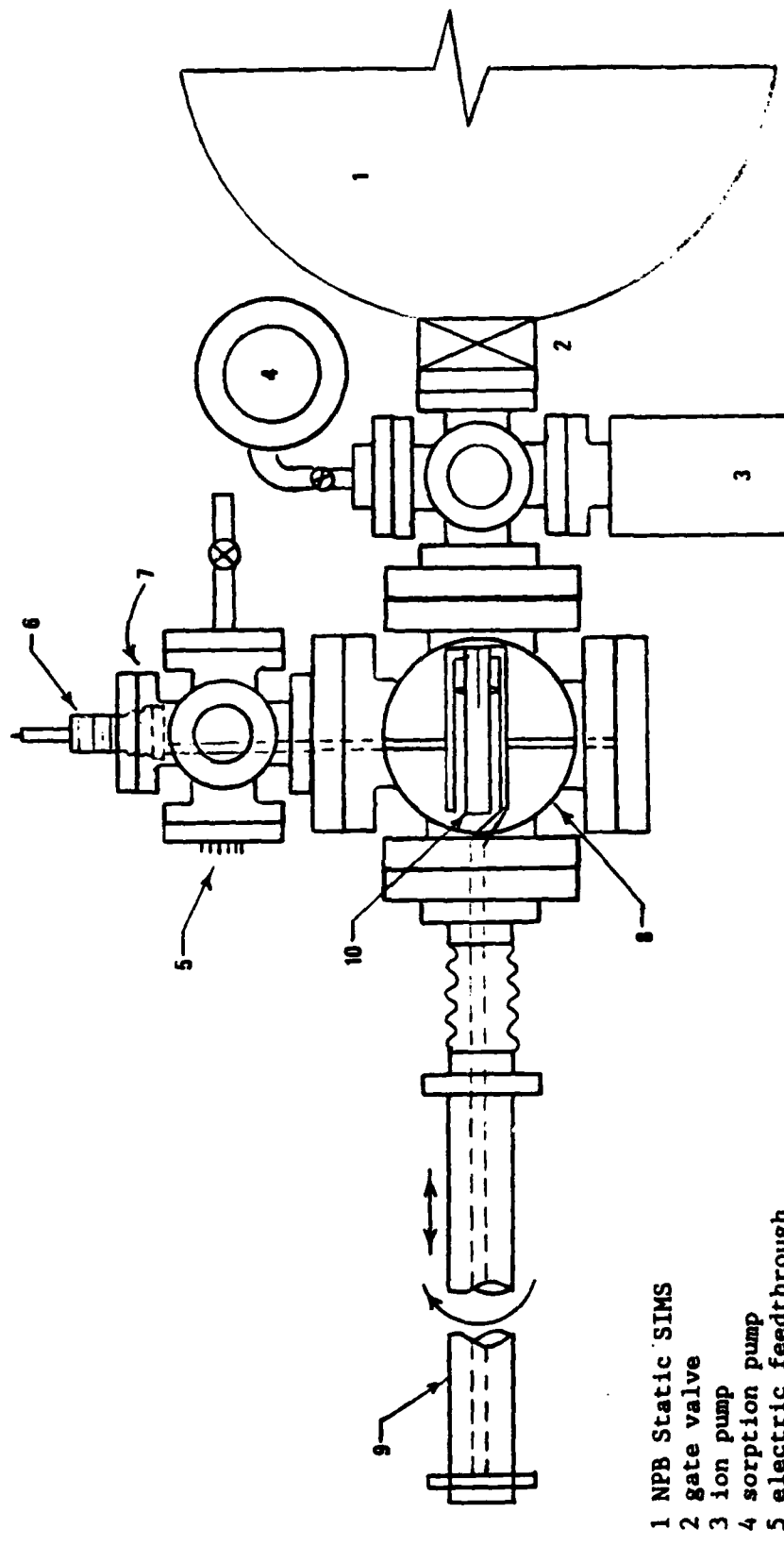


Figure 2a. Schematic diagram (front-view) of the chamber for slow crack measurements and/or preparation of fracture surfaces; this chamber attaches to the NPB-static SIMS (in Figure 1) at the gate valve (5).

Double Cantilever Beam Specimen

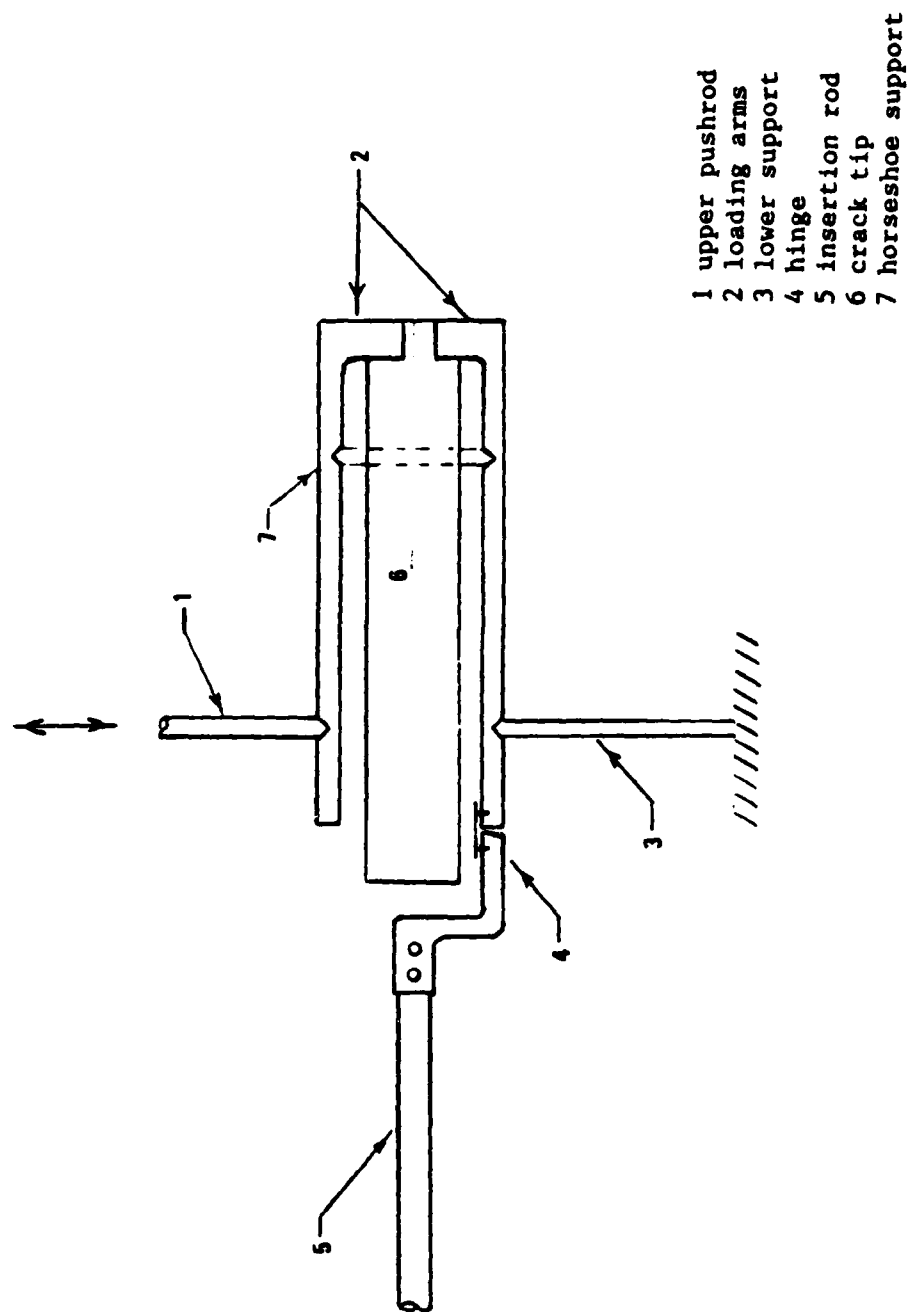


Figure 2b. The loading arrangement and double cantilever beam fixture for crack growth (item 10 in Figure 2a).

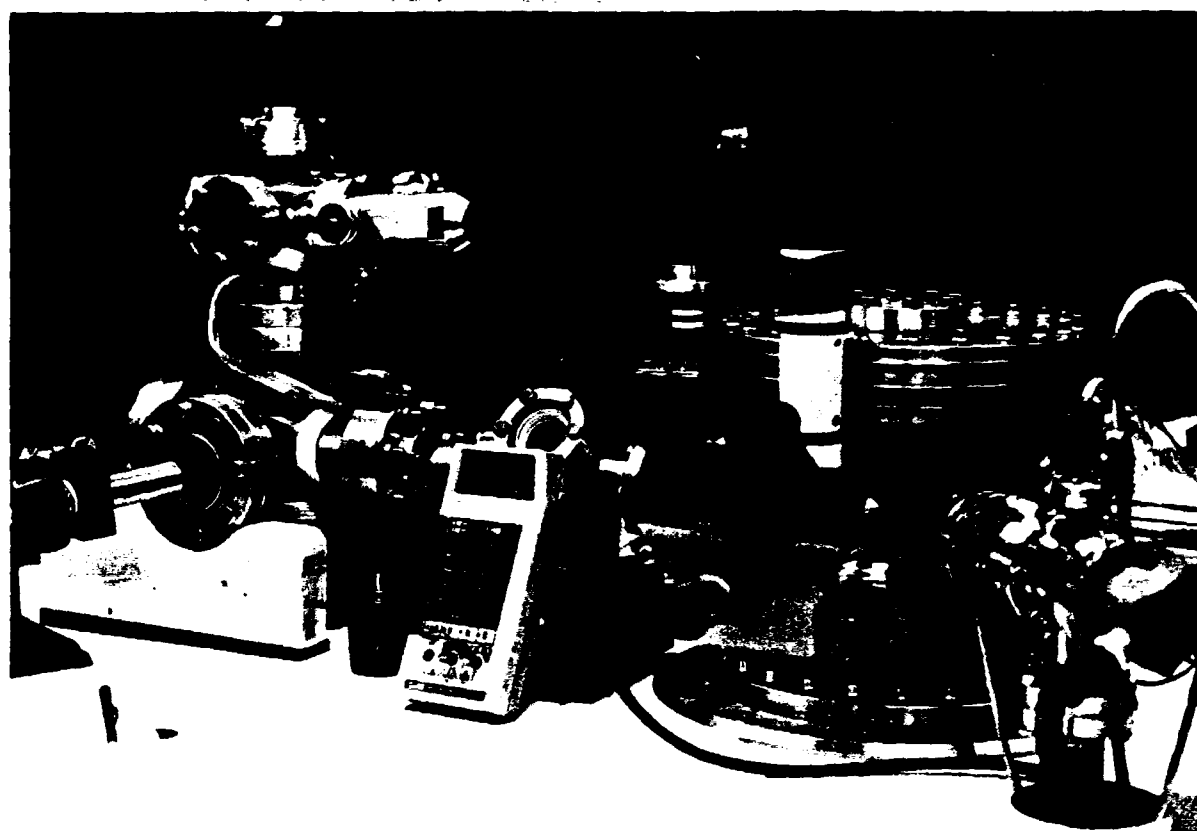
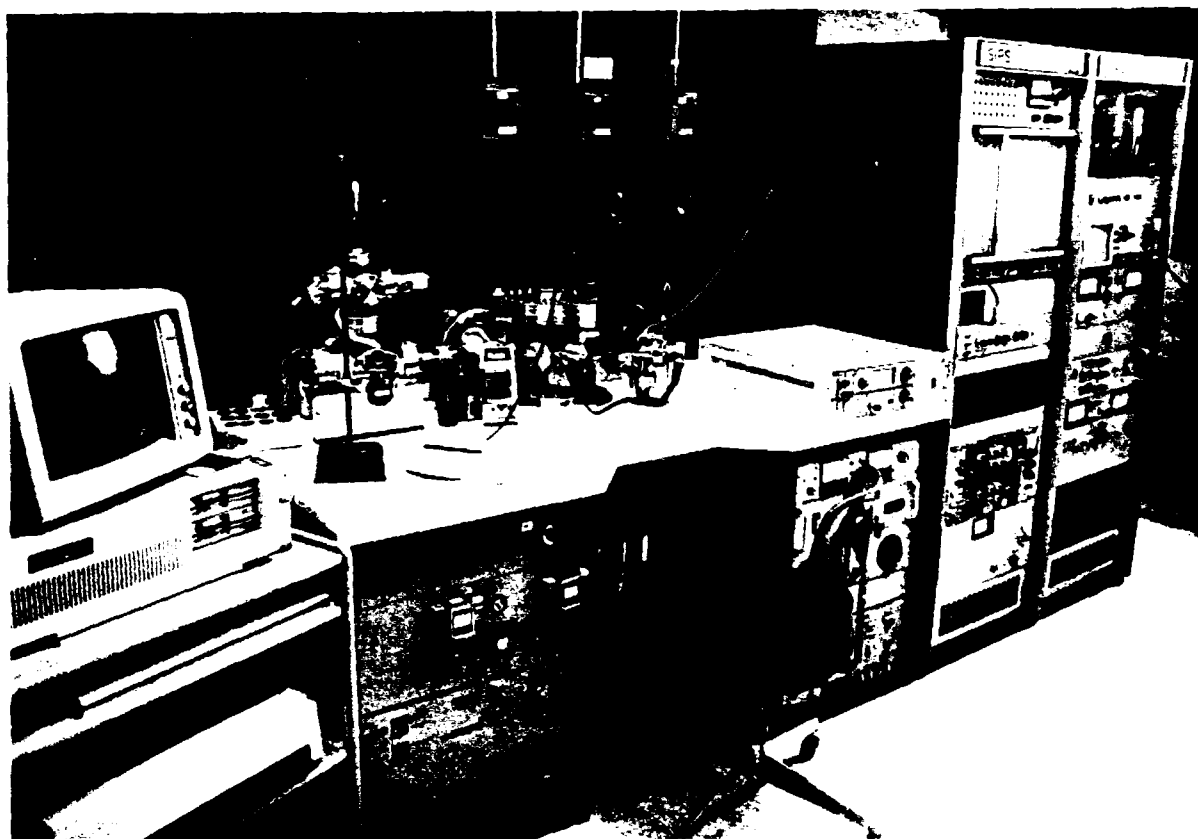


Figure 3a. Photographs of the NPB-static SIMS system.

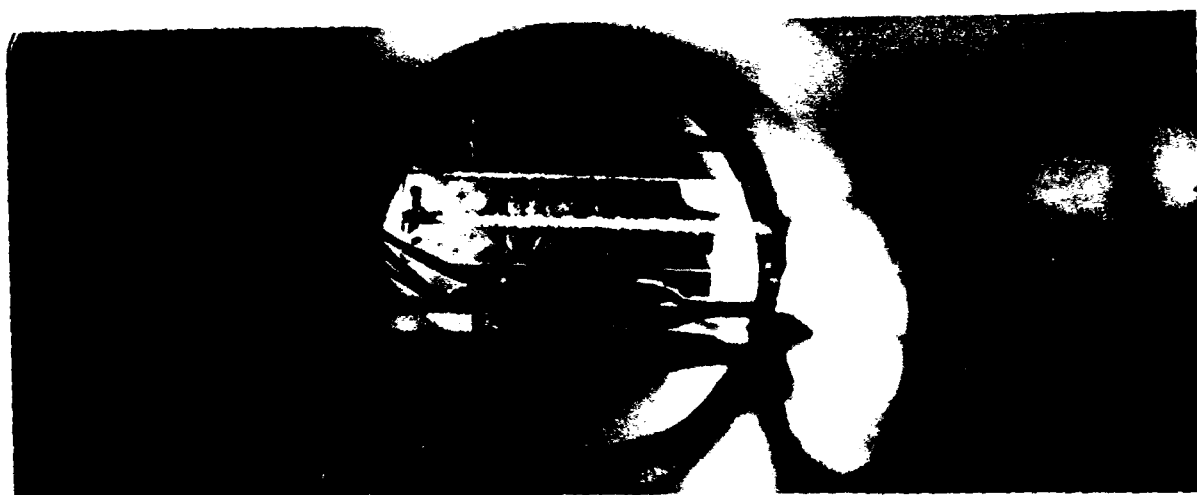
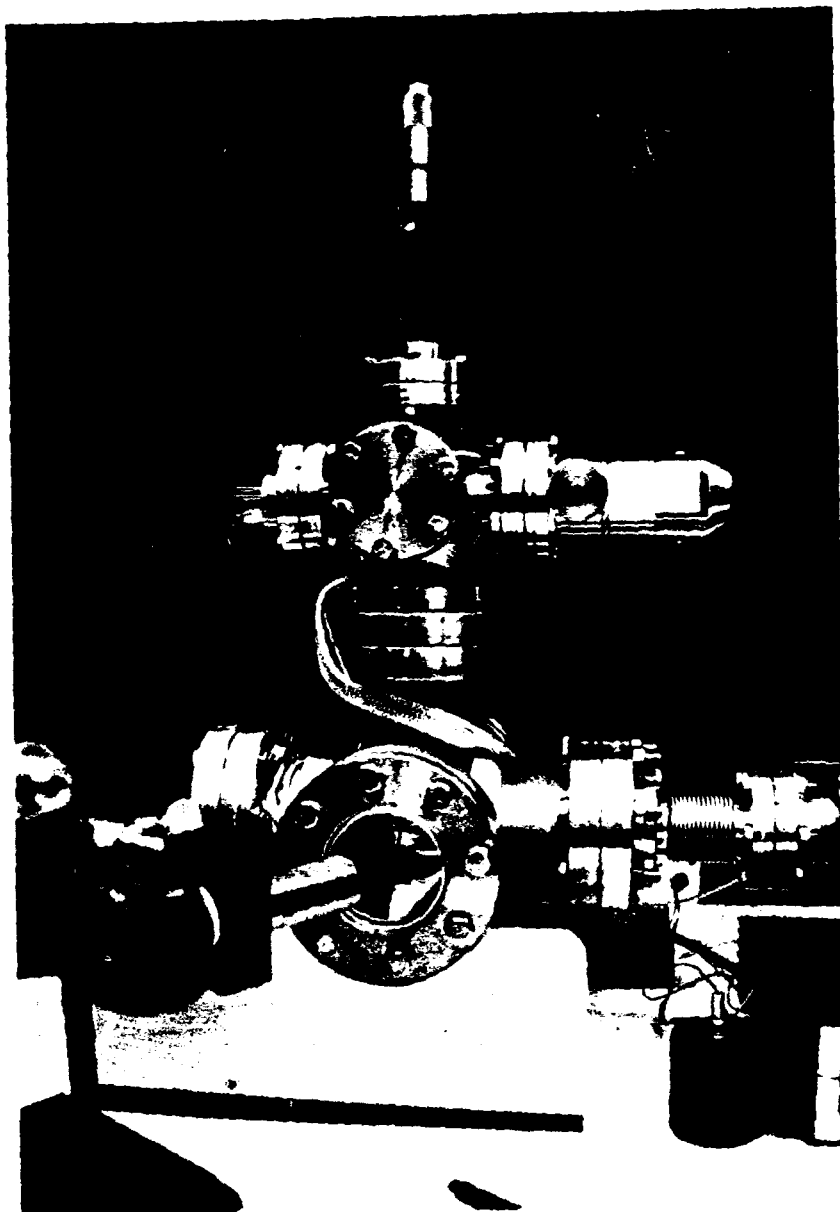


Figure 3b. Photographs of the slow fracture chamber and double cantilever beam specimen.

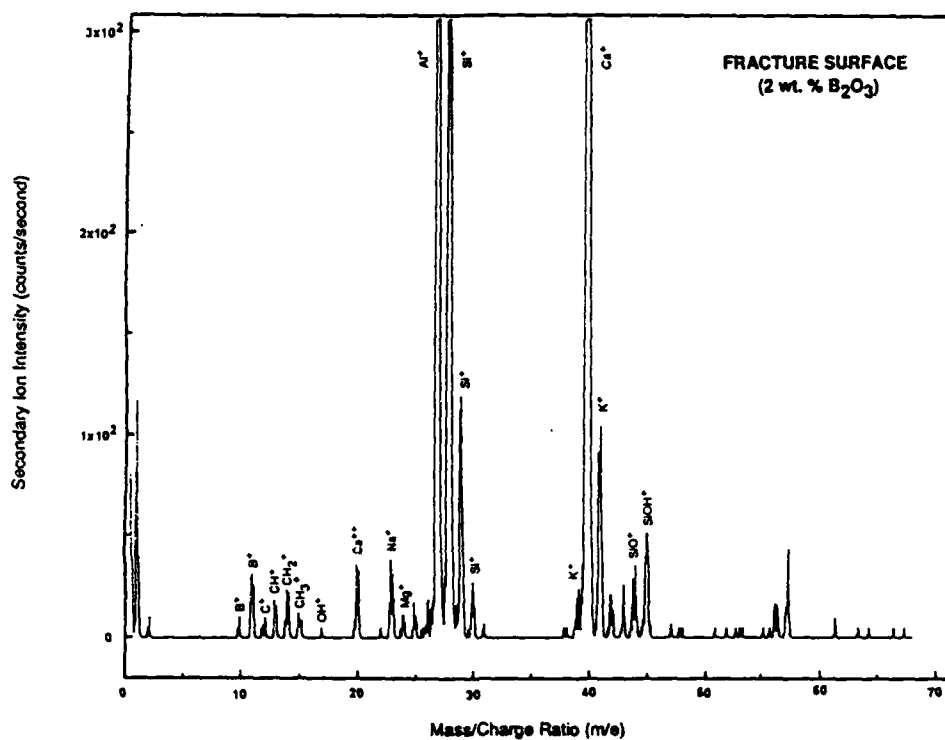
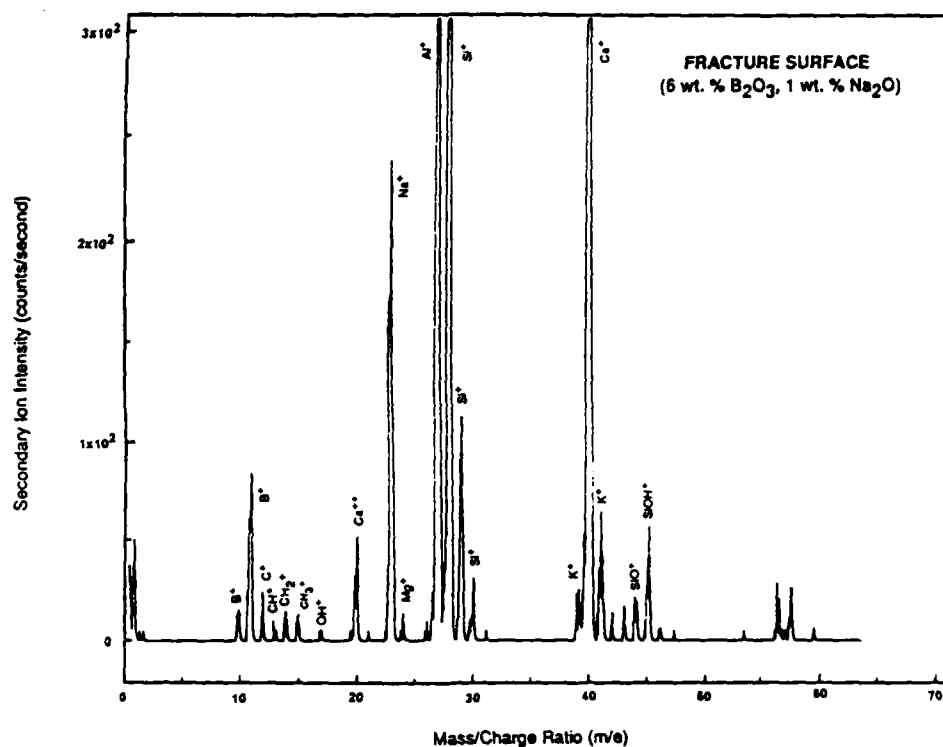
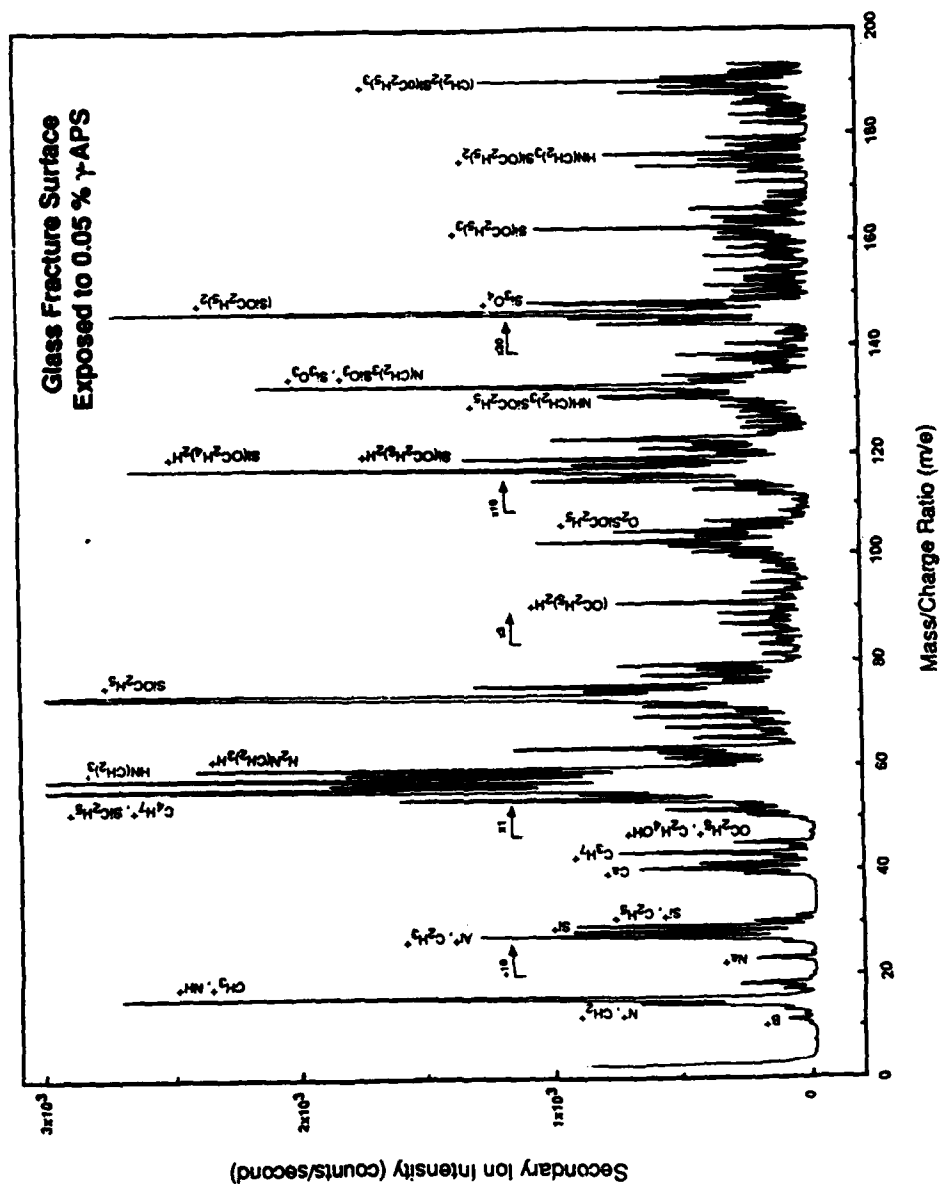


Figure 4. Static-SIMS spectra which demonstrate the ability to detect monolayer levels of hydroxyl and organics; comparison of the spectra reveals the sensitivity to trace levels of Na_2O and low concentrations of B_2O_3 .



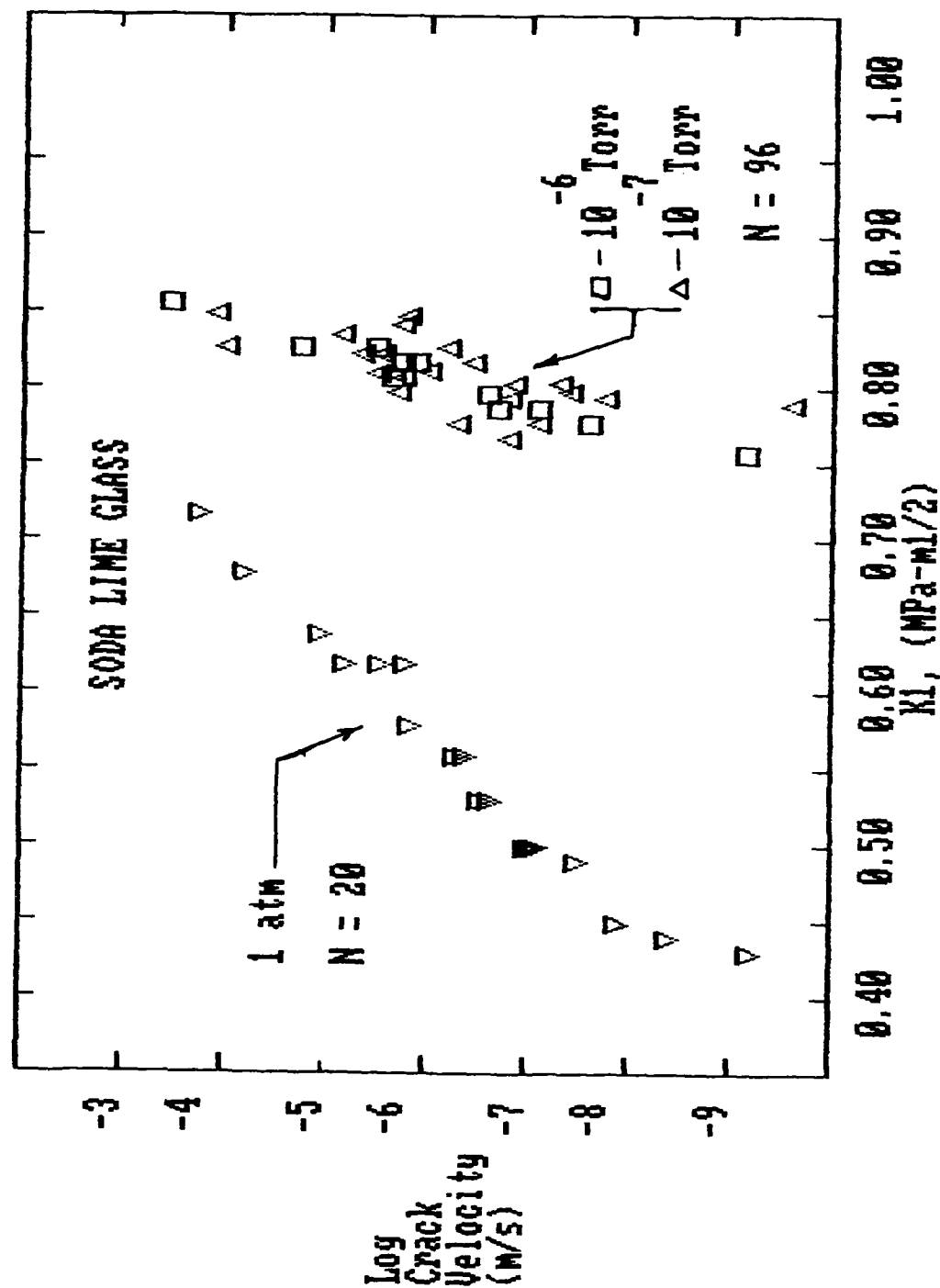


Figure 6. Crack velocity-stress intensity (V-K) measurements on a soda-lime glass obtained in the NPB-static SIMS system at 10^{-7} , 10^{-6} and 760 torr.

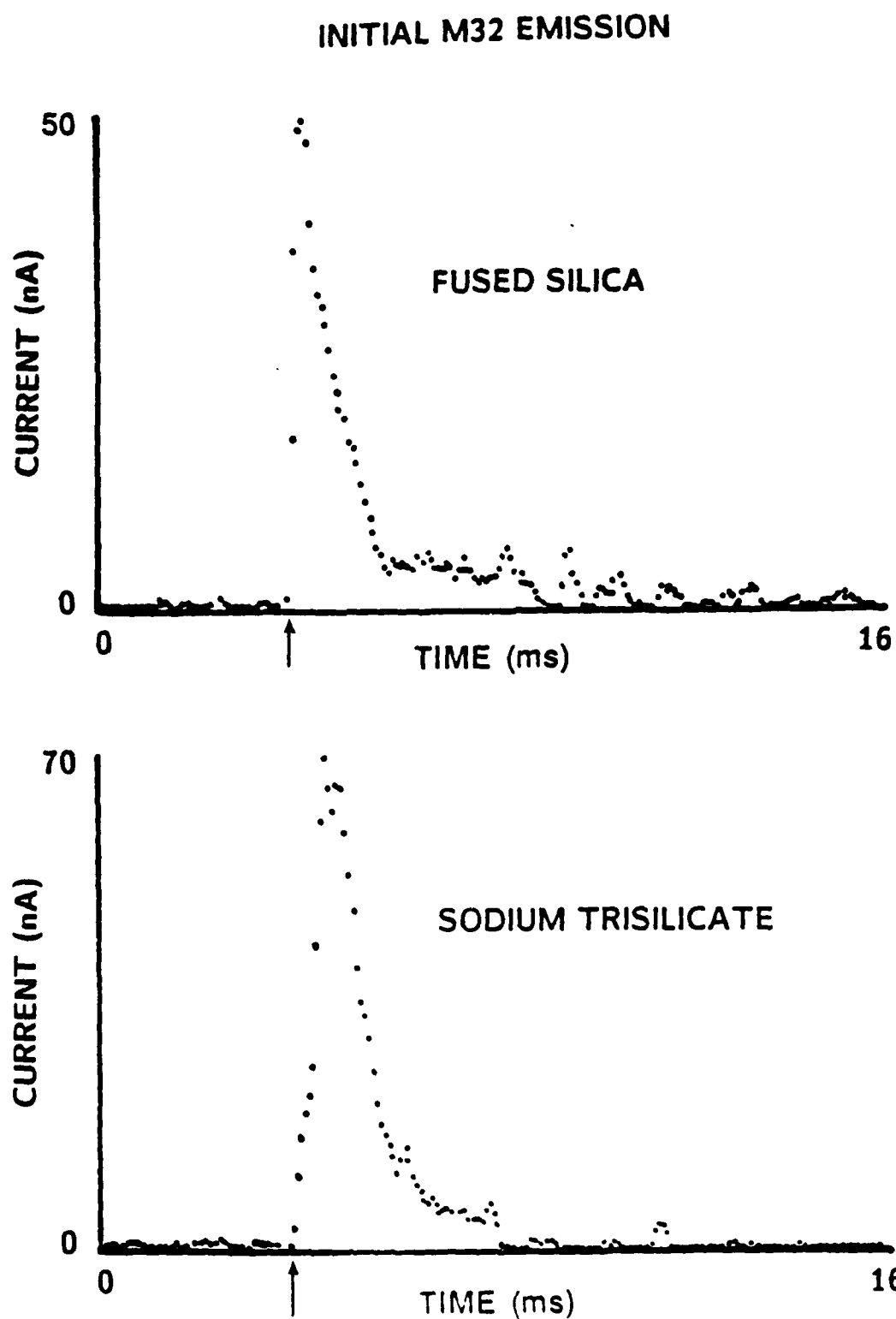


FIGURE 7. The neutral O_2 emission ($m/e = 32$) upon impact fracture of silica and sodium-silicate glasses; the arrows denote the onset of fracture.